Feature Article

Compatibilization in bio-based and biodegradable polymer blends

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ABSTRACT

The production and use of biopolymers increases continuously with a very high rate thus all information on these materials is very important. This feature article first defines the terms used in the area then discusses the distinction between degradation and biodegradation as well as their importance for practice. Biopolymers often have inferior properties compared to commodity polymers. Modification is a way to improve properties and achieve property combinations required for specific applications. One technique is blending which allows considerable improvement in the impact resistance of brittle polymers. However, further study is needed on the miscibility–structure–property relationships of these materials to utilize all potentials of the approach. The chemical structure of biopolymers opens up possibilities to their reactive modification. Copolymerization, grafting, trans-esterification, the use of reactive coupling agents have all been utilized with success to achieve polymers and blends with improved properties. Several examples are shown for the various approaches and their outcome. Biopolymers and their blends are applied successfully in several areas from agriculture to consumer goods, packaging and automotive.

Contents

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1. Introduction

Following a mild decline as a result of the 2008 financial crisis, the production of plastics increases continuously, and in 2010, it reached the value of 265 Mt worldwide and 57 Mt in Europe [1]. In the same year, European plastics converters processed 46.4 million tons into products, approximately 40% of these being short service life applications, mainly for packaging purposes, resulting in 24.7 Mt of post-consumer waste [1]. Not surprisingly, the related environmental concerns have also increased in recent decades strengthening efforts to reduce the ecological effect of polymeric materials. In 2009, for the first time in Europe, the amount of plastics waste utilized exceeded the amount going into landfills. This favorable tendency continued in the next year as well with 6 Mt being recycled into new products, 8.3 Mt converted into energy and 10.4 Mt deposited in landfills [1]. For the treatment of certain waste streams, however, composting proved to be the most advantageous method [2], thus biodegradable and compostable polymers have also found application in various fields.

Although the time-scale of the process is often disputed, a consensus has been reached regarding the prospective depletion of petrochemical feedstock [3,4]. Similarly to other areas, the plastics industry started looking for alternative sources of raw materials in the last few decades, and considerable interest is shown in natural, renewable solutions. Bio-based polymers, i.e. polymers produced from renewable feedstock, biomass in general, might replace fossil sources and also have considerable environmental benefits like decreased carbon-dioxide emission.

Although the term "biopolymer" is used in several different ways depending on the application area, the generally accepted definition covers polymers that belong to the abovementioned categories, i.e. are either renewable-based, biodegradable or both. The global production capacity of these materials shows dynamic growth [5,6]. Both environmental concerns and market trends stand behind this tendency, since with increasing oil prices, conventional polymers will become more and more expensive. Consumer expectations cannot be neglected either, since many customers take into consideration the environmental effect of the products they buy. The ratio of biodegradable polymers compared to non-degradable bio-based types has also increased recently [5]. One of the reasons leading to this trend might be the considerable changes in legislation related to compostable products in recent years. Long-term predictions, however, forecast the dominance of non-degradable biopolymers [5].

The relative importance of bio-based and biodegradable grades in polymer production might further increase in the future as production technology improves and becomes more cost-effective. According to various estimates, only less than 4% of world biomass is utilized by humanity, the majority for food-related, while only a fraction for chemical applications and plastics production [6] indicating that tremendous room exists for the further increase of capacity yet.

Biopolymers have much potential and several advantages, but they possess some drawbacks as well. In spite of increasing production capacity, they are still quite expensive compared to commodity polymers and their properties are also often inferior, or at least do not correspond to the expectation of converters or users. Although natural polymers are available in large quantities and are also cheap, their properties are even farther from those of commodity plastics. As a consequence, biopolymers must be often modified to meet the expectations of the market.

To utilize their potentials and penetrate new markets, the performance of biopolymers must be increased considerably. Consequently, the modification of these materials is in the focus of scientific research. In contrast to the development of novel polymeric materials and new polymerization routes, blending is a relatively cheap and fast method to tailor the properties of plastics. As a result, this approach may play a crucial role in increasing the competitiveness of biopolymers. In our present paper, we attempt to give a summary of recent trends and achievements in the field of biopolymer blends, with particular focus on miscibility–compatibility–property relationships.

2. Definitions, classification

As mentioned in the introductory part, the term "biopolymer" refers to polymers that are bio-based, biodegradable or both. Before discussing the various aspects of biopolymer blends, we define these categories in this section to help the understanding of subsequent discussion.

2.1. Biopolymers

Replacement of fossil feedstocks with renewable ones is one of the main endeavors of modern plastics industry. Natural polymers represent a specific class of materials among polymers based on natural resources. These occur in nature as macromolecules and we also include the physically or chemically modified natural polymers into this

category. Typical examples are cellulose, hemicelluloses, lignin, silk and starch. Another class of materials consists of the natural-based or bio-based synthetic polymers, the monomers of which are derived from renewable resources. Poly(lactic acid) (PLA) as well as bio-based conventional polymers like polyethylene (PE), poly(ethylene terephtalate) (PET) and polyamide (PA) belong to this category, while bacterial polyesters can be considered both natural and natural based materials, since the polymer is produced by bacterial fermentation, although in an industrial process. Biodegradability, on the other hand, is independent of the categories mentioned above, thus biodegradable polymers are not necessarily of natural origin.

The conditions for the determination of the bio-based content of polymeric materials are described in the European standard CEN/TS 16295:2012. The approach is based on the amount of bio-based carbon as a fraction of the total organic carbon content. Legislative details and exact protocols for the determination, however, must be elaborated in the future.

2.2. Degradation, biodegradation

Every polymer degrades to some extent on a certain time-scale depending on environmental conditions. However, precise definition of this characteristic is needed to obtain a useful description of polymer degradation. According to the related standard (CEN/TR 15932:2010), those polymers can be called degradable in which degradation results in the decrease of molecular weight through chain scission in the backbone and degradation goes to completion, i.e. the end products are low molecular weight compounds and biomass (mineralization and bioassimilation). Neither the mechanism of chain scission nor the environmental effect of the end-products is considered.

In biodegradable polymers on the other hand, chain scission is caused by cell (human, animal, fungi, etc.) activity, thus it is an enzymatic process, although it is usually accompanied and promoted by physicochemical phenomena as well. The two types of processes, i.e. physical and enzymatic, cannot be distinguished and/or separated in general, their combined effect leads to the complete degradation of the polymer (CEN/TR 15932:2010). The laboratory evaluation and testing of the biodegradability of polymeric materials is well defined in European standards (EN ISO 14851:2004, EN ISO 14852:2004, EN ISO 17556:2004, EN ISO 14855-1:2007/AC:2009, EN ISO 14855-2:2009). The tests are based either on the measurement of oxygen demand or on the amount of carbon dioxide evolved in the process. It is worth to note that most polymers containing various agents promoting degradation (oxo-biodegradable polymers) [7,8] cannot be considered biodegradable according to the standards mentioned above. Although their fragmentation and disintegration might take place, degradation is never complete among the testing conditions which simulate natural environments (soil, water, and compost). The environmental effect of the residual high molecular weight fractions is not satisfactorily described, and thus gives cause for serious concern. Consequently, these agents might help to solve the esthetic problems of pollution, but not the basic issue arising from the slow degradation of synthetic polymers. The use of such plastics had been widespread and encouraged in the past by imperfect legislation. Early standards (ASTM D3826 – 98(2008)) determined a certain decrease of tensile strength as the condition of degradability, which can be easily achieved by using pro-oxidants, for instance, without any real environmental advantage.

Unlike biodegradability, the determination of compostability relies on a very practical approach (EN ISO 14995:2006, EN ISO 13432:2000/AC:2005). Compostable materials have to show a high degree of biodegradation and disintegration (EN ISO 20200:2005) on a limited time-scale among composting conditions, without any harmful effect on the composting process or compost quality. Furthermore, the related standards refer to the compostability of the whole product and not that of the components (EN ISO 13432:2000/AC:2005), thus several factors, like the effect of different fillers on the degradation rate of biopolymers [9] have to be considered here. Legislation supporting plastic products with more advantageous environmental impact is more and more based on compostability; a favorable change considering that from the practical point of view degradability is only beneficial, if a product is also composted. In a landfill, even the degradation of natural materials such as paper and cardboard tends to be very slow. On the other hand, the physical recyclability of biodegradable polymers is often hindered by the considerable decrease of molecular weight during their melt state reprocessing. For example, poly(lactic acid), and most polyesters are prone to intra- and inter-molecular trans-esterification and hydrolysis during multiple processing cycles [10]. The controlled solvolysis – hydrolysis or alcoholysis – of polyesters, i.e. chemical recycling, however, might be a convenient way to convert plastic waste into valuable monomers and other feedstock chemicals [11]. Consequently, biodegradability and compostability are not always favorable, although they might be advantageous and should be applied for the management of certain plastic waste, e.g. from food packaging or agriculture [2]. However, the attention must be called here to the fact that selective collection and proper separation of waste streams is a basic condition of their successful treatment and utilization.

2.3. Types, properties and application of biopolymers

Fig. 1 presents worldwide biopolymer production capacities according to polymer type [5] indicating that starch and its blends, poly(lactic acid) and various types of polyhydroxyalkanoates (PHAs) (Fig. 2) are of the highest importance among bio-based and biodegradable polymers. The production of conventional polymers such as PE or PET based on renewable resources also gains more and more importance. These are not biodegradable, but their performance is the same as that of their fossil-based counterparts, thus bio-based conventional polymers might present a viable alternative, if they become cost competitive in the future.

Based on company announcements, by 2020 the most important bio-based polymers will be starch (1.3 Mt), PLA (0.8 Mt), PHAs (0.4 Mt) and bio-based PE (0.6 Mt) [6].
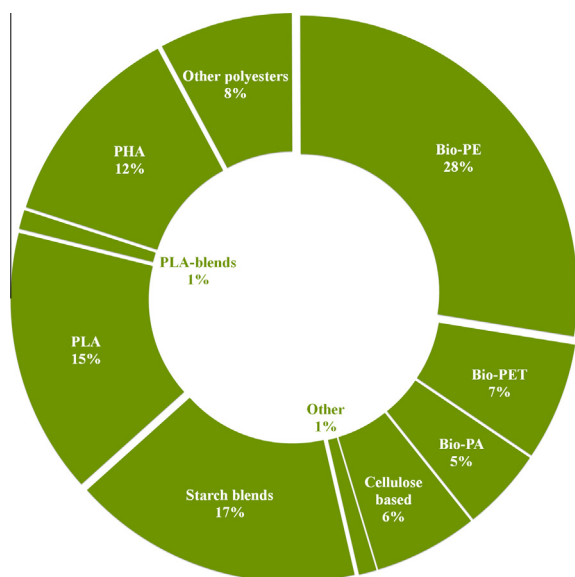
Fig. 1. Worldwide biopolymer production capacities in 2010 according to polymer type. [5].

In this paper, we focus our attention on the most significant biopolymers which are both bio-based and biodegradable, i.e. starch, PLA, poly(3-hydroxybutyrate) (PHB) and their blends. While the stiffness and strength of these are usually large, their application is often limited by processability, sensitivity to water and low impact resistance. In the case of starch, one of the most abundant biopolymers, these deficiencies are generally overcome by plasticization,

although other approaches are also common. Poly(lactic acid) received much attention in recent years [12,13], as one of the most promising alternatives to conventional plastics. Its mechanical properties are comparable to those of polystyrene and it is used in increasing quantities in packaging applications, as a consequence [14]. On the other hand, several drawbacks limit its widespread use like processing difficulties, low heat resistance and high cost, while its rapid physical aging results in a brittle material with low impact resistance [15]. The most common representative of PHAs, poly(3-hydroxybutyrate), is also a brittle polymer, as its enzymatic polymerization leads to the formation of macromolecules with highly ordered stereochemical structure, thus large crystallinity [16]. Economic aspects are very important as well. Although increasing capacities result in the reliable production and decreasing price of biopolymers, their cost still exceeds that of most commodity polymers. For all these reasons, biopolymers are generally used in modified forms like blends, composites or plasticized grades. The modification of biopolymers by blending with other bio-based and/or biodegradable materials has many advantages, since it offers an option to adjust properties in a wide range, while legislation also favors completely compostable materials with minimal carbon-footprint. Quite a few commercial grades exist already, but we must emphasize that successful blends cannot be produced without proper compatibilization.

3. Modification approaches

In order to adjust the properties of biopolymers to the intended application, a wide variety of approaches are used for their modification, like plasticization, the
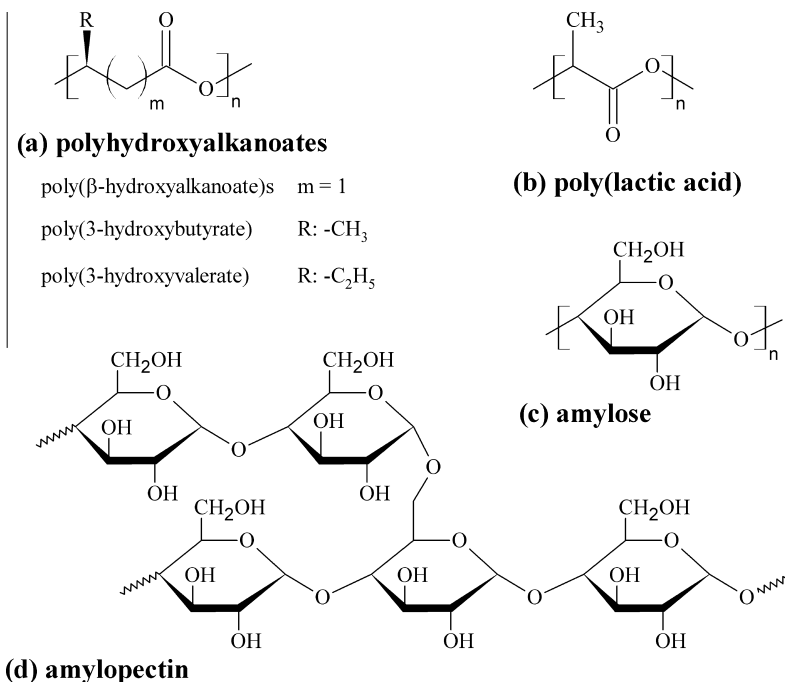

Fig. 2. The chemical structure of the most important biopolymers: (a) polyhydroxyalkanoates; (b) poly(lactic acid); (c and d) the main components of starch, amylose and amylopectin, respectively.

incorporation of fillers and reinforcements, blending and impact modification. Several of these will be introduced briefly in this section, while blending and compatibilization will be discussed more in detail in subsequent parts of the paper.

3.1. Plasticization

Plasticization is often used for the modification of biopolymers to improve their processability and/or other properties demanded by a specific application. Plasticizers exchange the intermolecular bonds among polymer chains to bonds between the macromolecules and the small molecular weight compound thus promoting conformational changes resulting in increased deformability. Both the glass transition and the processing temperature of the material decrease, thus enabling the melt processing of heat-sensitive polymers, like poly(3-hydroxybutyrate), at lower temperatures [17].

The melt processing of starch is impossible without gelatinization, i.e. destroying the crystalline structure of native starch by the use of a plasticizer [18,19]. The material obtained in this way is referred to as thermoplastic starch (TPS). The nature and concentration of the plasticizer strongly influence the rheological and mechanical properties of TPS. Neat starch has a high glass transition temperature, and its relative large modulus and strength is accompanied by poor deformability and impact resistance due to the limited conformational mobility of its stiff chains [20]. Elastomeric behavior would be advantageous for several applications, which can be achieved, among other methods, by decreasing T_g below ambient temperature via plasticization [21].

Numerous studies and patents describe the plasticization of starch using either low molecular weight or polymeric compounds [21,22]. The plasticizers applied are mainly low molecular weight polar compounds such as water, glycerol, urea and formamide [22]. However, as in their elaborate work Lourdin et al. [21] point out, TPS is always a ternary system, since the water content of plasticized starch should always be taken into consideration. In plasticized starch the effect of water depends on the nature and concentration of the plasticizer and on relative humidity, and water content affects the macroscopic properties of TPS to a great extent. Recently, using state of the art visualization techniques Paes et al. have shown [23] that moisture content and interaction with water determines the fracture mechanism in cassava starch films as well as in gelatin and hydroxypropyl cellulose. Although water is a very efficient plasticizer for starch too, usually compounds with higher boiling point are preferred because they decrease water sensitivity and lead to more stable properties [19].

A similar approach can be applied for the modification of poly(lactic acid). Usually the application of PLA is not limited by its processability, but by its mechanical properties. Plasticization is one approach to overcome the stiffness and low impact resistance of the polymer [24]. Several compounds have been identified as possible plasticizers for PLA, e.g. different esters [25–27], glycerol [14],

poly(ethylene glycol) (PEG) [14,27–29] and oligomeric lactic acid [14].

Since the properties of poly(hydroxy alkanoate)s can be efficiently and conveniently tailored by controlling the comonomer ratio during polymerization via fermentation [16], plasticization is not a widespread approach for their modification. However, plasticization should not be neglected as a non-expensive option to improve the toughness of the inherently stiff poly(3-hydroxylbutyrate). Combined with conventional copolymerization, the deformability of the material can be increased considerably by this route [17,30].

Miscibility is an important issue in plasticization, since plasticizers tend to migrate to the surface of the products raising environmental and health issues, as well as altering the macroscopic properties of the material as an effect of changing plasticizer content. Migration can be hindered by increasing the molecular weight of the plasticizer, which leads to slower diffusion indeed, but it results in a decrease of miscibility and efficiency as well [24]. Another innovative solution to this problem might be the grafting of plasticizer molecules to the polymer chain by reactive processing [26,31–33].

3.2. Physical blending

Under the term physical blending we understand the simple mixing of polymeric materials in the melt state with no chemical reactions taking place. It is a convenient route to create new materials with the desired combination of properties. Blending can be carried out by using conventional machinery, i.e. no expensive investment is necessary, which is an important aspect for industry. A very wide range of properties can be achieved by this approach to meet the requirements of the targeted application in relatively short time and for low cost compared to the development of new monomers and polymerization techniques.

The goal of blending might be the improvement or tailoring of properties to a certain application, or as it is often described, maximization of the performance of a material. However, the specific, primary motivation of blending could be much more diverse. Table 1 gives a summary of these: cost reduction [14,19,34–49], the improvement of mechanical properties generally [44,45,48–53], and impact resistance particularly [14,54–68], or the decrease of sensitivity to water [49,50,53,55,69] are all common aims. The different approaches applied in the case of different polymers reveal the most significant characteristics to be improved. PHAs are very versatile, but also expensive, thus not surprisingly their modification via blending often involves starch and aims the reduction of material costs. The same approach can be observed in the case of PLA as well, although the improvement of toughness via incorporating elastomeric polymers seems to be somewhat more important. On the other hand, the price of starch is low, but its mechanical properties are inferior and it is sensitive to water, thus the improvement of these characteristics is of high importance. In all these cases however, successful blends should either offer similar performance as the

Table 1
Biopolymer blends: types and aims of modification.

Base polymer	Second component	Aim			
		Cost reduction	Mechanical property	Toughness	Water sensitivity
PLA	PHAs		51	59–61	
	PCL			63, 65	
	NR			57, 58	
	Starch	34, 14, 40		14	
	PBS			62	
Starch	PA11		50		50
	PU			54, 55	55
	PHB		48, 49		49
	NR				
	PLA		52		
	PCL				
	PBS		53		53
PHB	Starch	41–49	44, 45		

starting material for a reduced cost or provide high added value.

The characteristics of brittle biopolymers are very much comparable to polystyrene (PS), a widely used commodity thermoplastic [24]. As limited impact resistance led to the development of numerous PS-based blends and copolymers in order to overcome this flaw, a similar trend is expected for PLA (○) and other biopolymers (■,●) as well (Fig. 3). It should also be emphasized that the annual number of publications related to PS-based blends (□) reached its zenith around 2004, while continuous increase of interest is shown in biopolymer blends.

3.3. Chemical approaches

Plasticization and physical blending offer convenient approaches to the modification of biopolymers, but
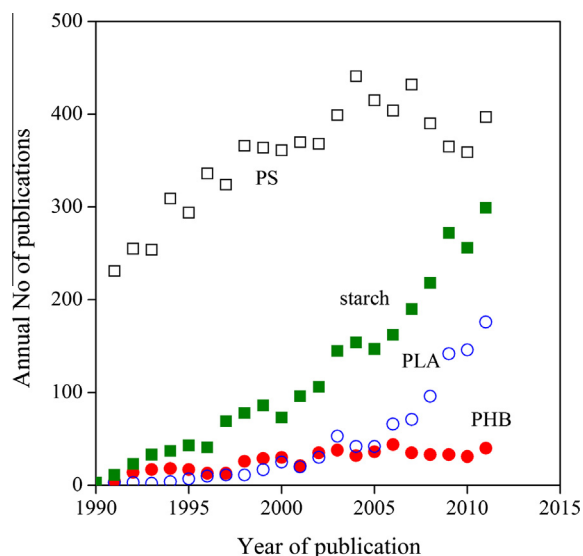

Fig. 3. The number of publications on the blends of poly(3-hydroxybu-tyrate) (PHB) (●), poly(lactic acid) (PLA) (○), starch (■) and polystyrene (PS) (□).

similarly to commodity polymers very few biopolymer pairs are miscible or even compatible with each other. As a consequence, chemical routes, i.e. the chemical modification of the components or reactive compatibilization are often used to achieve property combinations required in specific applications. A good example of chemical modification is the copolymerization of PHB.

With changing comonomer type and amount, the properties of polyhydroxyalkanoates can be modified in a relatively wide range [16]. Also, as Pellegrini and Tomka have proposed [70], the low degree of internal mobility of the polysaccharide chain in native starch can be greatly improved by esterification or trans-esterification with hydroxyalkanoates. Grafting, the preparation of block copolymers, or reaction with two or multifunctional compounds are convenient ways to modify biopolymers and improve their compatibility with others. The fact that many of these polymers are produced by stepwise polymerization and they also often possess reactive functional groups makes them suitable for reactive processing. This approach is often used in compatibilization and will be discussed in Section 5.2 more in detail.

4. Blends

The modification of polymers by blending is a mature technology developed in the 1970s or even earlier. A large number of papers and books were published on the topic [71–75], and the theoretical studies carried out mostly on commodity and engineering thermoplastics paved the way for industrial applications. As a result of these studies, the theories adapted from the mixtures of small molecular weight solvents to polymer solutions by Flory [76] found their way to polymer blends. Equation of state theories developed by Flory [76], Simha and Somcynsky [77], and Sanches and Lacombe [78] represent a theoretically more sound approach, but experiments necessary for validation and obtaining the parameters describing the interaction of the components, and miscibility generally, are overly complicated and did not find application in practice. Detailed studies on the most diverse polymers proved that most commercial polymers are immiscible and compatibilization is needed to achieve properties required for specific applications. A large number of commercial blends are available today and many of them also contain a compatibilizer [75].

The advent of biopolymers resulted in a revival of blending technology, as their several disadvantages can be overcome by blending, as described above. The number of papers on the blending of biopolymers is vast, partly because of the huge number and wide diversity of these polymers and partly because of the increased interest in them. PLA and starch are the most often studied materials, but one could mention poly(3-hydroxybutyrate-co-3-hydroxy-hexanoate)/poly(vinyl phenol) [79], thermoplastic phenol formaldehyde resin/poly(ε-caprolactone) (PCL) [80], PHB/PCL [81], PLA/poly(butylene succinate) (PBS) [82] poly(3-hydroxybutyrate-co-3-hydroxyhexanoate)/PLA [83], PHB/PLA [84], chitosan/soy protein [85], PHB/cellulose acetate butyrate [86], PLA/PEG [87], PHB/PBS [88], PLA/poly

(epichlorohydrin-co-ethylene oxide) (PEEO) [89], poly(pro-pylene carbonate)/poly(ethylene-co-vinyl alcohol) [90,91] without even attempting to be comprehensive. As mentioned above, the goals of blending are various from the modification of T_g, improvement of fracture resistance, flexibility, processability to the modification of some other properties like optical characteristics or flammability.

4.1. Factors determining properties

Similarly to commodity and engineering polymers, most of the biopolymer pairs are only partially miscible, thus form blends with heterogeneous structure. The properties of all heterogeneous polymer systems including particulate filled polymers, fiber reinforced composites and blends are determined by four factors: component properties, composition, structure and interactions. If possible, interactions are even more important in blends than in other heterogeneous polymeric materials since they determine the mutual solubility of the phases, the thickness and properties of the interphase formed during blending and the structure of the blend. As a consequence, the proper, and possibly quantitative, characterization of interactions is of utmost importance for the prediction of blend properties, but also for compatibilization.

4.2. Miscibility, compatibility

The miscibility theories mentioned above may help in the characterization of interactions. However, we must define first the terms often used in relation to polymer blends. In our interpretation, miscibility is a thermodynamic term which, with the help of an appropriate model, describes the behavior of a polymer pair by specifying the number of phases and their composition forming upon blending. The model most frequently used for that purpose is the Flory–Huggins lattice theory [92,93]. On the other hand, compatibility is a technical term defining the property profile of the blend in view of a certain application [94]. If the combination of properties is advantageous and corresponds to the expectation, the compatibility of the polymers in question is good, and they are incompatible when properties are not acceptable. The compatibility of polymer pairs is often modified by physical (compatibilizers, block copolymers) or chemical (e.g. reactive processing) means. Miscibility is often mentioned in papers dealing with the blends of bio-based and biologically degradable polymers, but rarely investigated properly. Phase diagrams and the mutual solubility of the components in each other are not determined, only the fact is established that either a homogeneous or heterogeneous blend forms. The conclusion is usually based on the number of glass transition temperatures detected or on the number of phases observed on SEM micrographs. However, all polymers are partially miscible and dissolve in each other to some extent, and mutual solubility depends on interactions, which can be characterized by the Flory–Huggins interaction parameter (χ), for example. Although interactions are complicated and the parameter is rather complex consisting of various components [95], the approach is the simplest from the practical point of view

and it is widely used for the estimation of miscibility [82,96–98].

The blends of biopolymers behave differently from those of commodity polymers and resemble more the engineering thermoplastics. They contain polar groups which can form stronger interactions through induced dipole or dipole–dipole interactions than, for example, the blends of polyolefins in which only dispersion forces act. As a consequence, the mutual miscibility of the phases is larger in biopolymers shown also by several papers in which complete miscibility was claimed at the end of the composition range up to as much as 10% or 20% of the dispersed component [87,99,100]. However, no attempt is made to determine the mutual solubility of the phases basically ever [101]. DSC and DMA is used practically in all studies and the T_g of the phases is determined [61,79,83,84,88,99–105]. Miscibility is often deduced from the fact that only a single T_g is detected in the blend [99,100], the value of which is between the glass transition temperature of the components. One example is shown in Fig. 4 in which the T_g determined in PLA/PHB blend is plotted against composition (○) [100]. We must call here the attention to the fact that if the difference between component T_gs is not large enough, more than 20–30 °C, most methods cannot detect separate glass transition temperatures even if the components are immiscible and the blend is heterogeneous. Very frequently two glass transitions are recorded which move towards each other with changing composition [89]. The results are usually evaluated only qualitatively and good interaction is deduced from the change in T_g in such cases. Such a combination (PLA/PEEO) is also shown in Fig. 4 as an example (□,■). However, such results can also be analyzed quantitatively, for example, by the approach of Kim and Burns [106] with which the mutual miscibility of the phases can be estimated reasonably well. Interactions are often studied also by FTIR
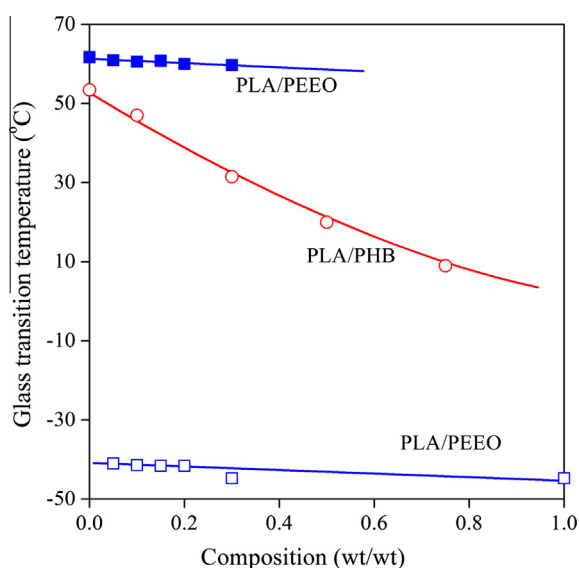

Fig. 4. Composition dependence of glass transition temperature in biopolymer blends [89,100].

spectroscopy [83,85,86,91,103,104,107,108]. Unfortunately, interactions between the components in biopolymer blends are usually not strong enough to detect any shift in the absorption band of characteristic groups. H-bonds are sufficiently strong to measure their effect, but they are present only in a limited number of polymer pairs. Even if interactions are detected by spectroscopic techniques, they are difficult to relate to interaction parameter, structure or properties.

We must also mention here studies focusing on the crystallization and crystalline structure of biopolymers. A large number of papers discuss miscibility and crystallization together [79,84,89,98,99,102], although the relationship is not always clear. Aliphatic polyesters, especially PLA, often have a low T_g and crystallize rather slowly. These two facts result in the cold crystallization of samples during DSC measurements. However, since the samples are amorphous under practical conditions, cold crystallization has no relevance to miscibility and properties. Modification, including blending and the incorporation of fillers, usually increases mobility, thus the behavior of the polymers during cold crystallization changes, but this behavior still does not offer quantitative information about interaction, miscibility and properties. On the other hand, interaction can be determined from changes in the melting temperature of the components by the method of Nishi and Wang [109]. The basis of the approach is the Flory–Huggins lattice theory. The approach always yields negative values for χ indicating miscibility, but the existence of the crystalline phase alone shows that blend structure is heterogeneous also in such cases. Nevertheless, the value of the interaction parameter, which ranges from -0.013 to -0.295 for polyolefin [110] and poly(vinylidene fluoride) (PVF$_2$)/PMMA [109] blends, respectively, gives a measure of the strength of interaction. Values of -0.089 and -0.15 were calculated for PHB/PEEO [98] and PLA/PBS [82] blends, respectively.

4.3. Properties

The properties studied in biopolymer blends vary in a wide range. T_g determined by DSC or DMA is one of the preferred characteristics, as discussed above. Mechanical properties like stiffness [87,91,104,111], strength [90,91,104,111], deformability and flexibility [89,100,102,111] are also often determined. One of the drawbacks of PLA is its stiffness and brittleness further enhanced by physical aging. Plasticization [87,108] and blending [87,108] are ways to improve flexibility to produce materials for packaging films. Similarly, rheological properties and processability [107,108,111] are also often improved by the same approach. Many attempts are done to improve the fracture and impact resistance of biopolymers by blending [14,54–68,89,111–113]. One example is given in Fig. 5 showing the tremendous increase in the impact resistance of PLA (●) upon the introduction of ethylene-co-vinyl acetate polymer. The improvement in impact resistance depends also on the vinyl acetate content of the copolymer showing the importance of interactions in the determination of blend structure and properties. Occasionally other properties like optical characteristics
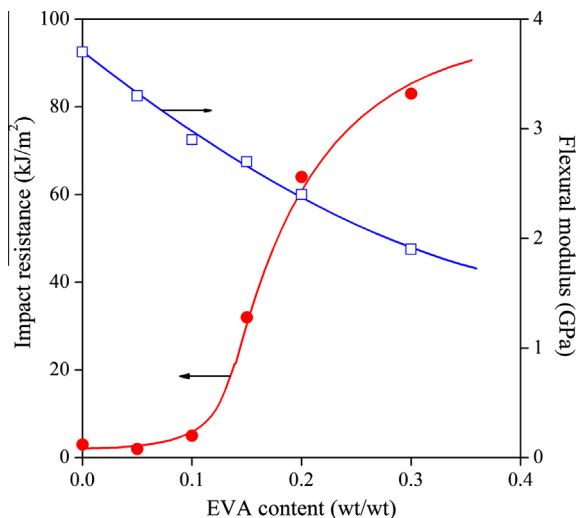

Fig. 5. Effect of poly(ethylene-co-vinyl acetate) on the mechanical properties of poly(lactic acid) [112].

[82,111], biodegradability [108,114,115], flammability [116] and price [14,19,34–49,117] are also determined and discussed in various publications.

4.4. Miscibility-structure–property correlations

Unfortunately very few papers deal with miscibility–structure–property correlations and even less do it quantitatively, although these correlations exist, and are important. As mentioned above, the strength of interaction can be characterized by the Flory–Huggins interaction parameter (χ), which in heterogeneous blends can be related to the size of the dispersed particles (r) [118]

$$r = \frac{4\alpha\gamma_{AB}f(\eta_{rel})}{\pi\eta_m}\varphi_d \tag{1}$$

where α is the coalescence probability of particles, γ_{AB} interfacial tension, $f(\eta_{rel})$ is function of the relative viscosity of the components, η_m is viscosity of the matrix and φ_d is the volume fraction of the dispersed phase, and to the thickness of the interphase [119]

$$\ell = \frac{b}{\chi^{1/2}} \tag{2}$$

where b is the effective length of the monomer. Mechanical properties, yield stress and tensile strength in particular, strongly depend on miscibility and structure. The composition dependence of tensile strength can be expressed as

$$\sigma_T = \sigma_{T0}\lambda^n\frac{1-\varphi_d}{1+2.5\varphi_d}\exp(B_T\varphi_d) \tag{3}$$

where σ_T and σ_{T0} are the true tensile strength ($\sigma_T = \sigma\lambda$, $\lambda = L/L_0$) of the heterogeneous polymeric system (blend or composite) and the matrix respectively, n is parameter reflecting the strain hardening characteristics of the matrix and B_T is related to the load bearing capacity of the dispersed phase [118,120,121]. This latter is determined by

interaction as well as the inherent properties of the components:

$$B_T = \ln\left(C\frac{\sigma_{Td}}{\sigma_{T0}}\right) \qquad (4)$$

where σ_{Td} is the strength of the dispersed phase, while C is related to the stress transfer between the phases, i.e. interactions, and was found to be in inverse correlation to the Flory–Huggins interaction parameter [118], as presented for a number of polymers in Fig. 6. The value obtained for the biopolymer blend PLA/PBS (●) [82,122], which was calculated from results taken from the literature, is also plotted for comparison. The figure clearly shows the importance of interactions in the determination of the mechanical properties of biopolymer blends, but also the universality of the correlation.

4.5. Specific blends

A large number of blends prepared, studied and reported in the literature have been listed in the introductory part of Section 4. In this section we discuss two groups of blends, which seem to have special significance, more in detail. Starch blends merit more attention because of their complexity, while the impact modification of PLA has large practical importance. When discussing biopolymers, material cost is always of high importance: the price of these materials generally exceeds that of commodity plastics considerably, thus hindering their application. One exception is starch, a non-expensive, abundant biopolymer, which is applied more and more often for the preparation of blends and composites. It is widely used to decrease the price of other bio-based or biodegradable polymers such as PLA [14,19,34–36,38,39] or polyhydroxyalkanoates [41–49].

Two approaches are used to prepare starch based heterogeneous systems. The first uses neat [41,43,44,69,116,123,124]
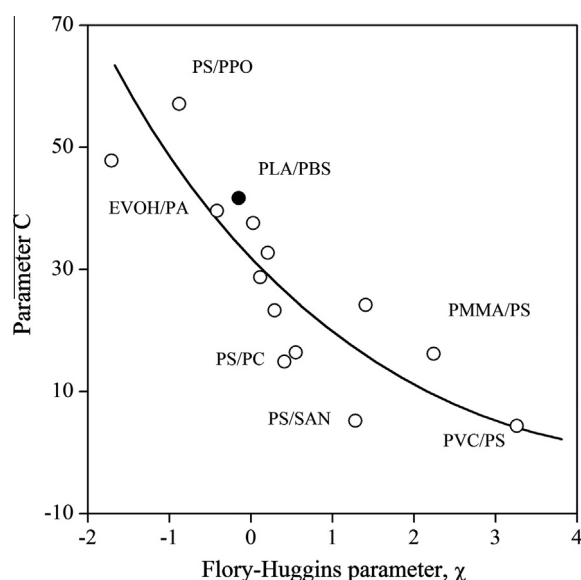

Fig. 6. Correlation of parameter *C* related to stress transfer and the Flory–Huggins interaction parameter in polymer blends [82,118,122].

or chemically modified starch [115] in powder form for the preparation of composites. As the strong hydrogen bonds in native starch hinder the dispersion of these particles in a polymer matrix both on microscopic and on molecular scale, these materials can be considered more as composites rather than blends and they often possess very poor properties. Several blends of starch with conventional polymers have been reported as biodegradable materials in previous decades, although they do not satisfy the present requirements of biodegradability. The approach failed already in the 1960s and 1970s, since starch degrades indeed, but the polymer seldom, except when a biodegradable matrix polymer is used for blending. The other approach is the use of thermoplastic starch (TPS) produced by plasticization using water or glycerol [45,46,48], which offers much better properties [48].

Commercial blends of biopolymers and starch are available on the market. However, the decrease of cost achieved by blending with starch is usually accompanied by disadvantageous changes in other characteristics. Generally, if a polymer is not miscible with starch, blending can be expected to result in inferior mechanical properties compared to both components. Even in the case of rather good compatibility, the addition of starch usually degrades the characteristics of the other polymer. Consequently, the most common goal of blending with starch is to minimize costs, while maintaining an acceptable combination of properties. As emphasized above, interactions and structure are extremely complicated in such blends, since the plasticizer is partitioned among the components changing properties considerably and making any kind of prediction very difficult. Very often, compatibilization is needed, which further complicates structure–property correlations [115,125].

The blending of brittle biopolymers with elastomers gives an option to create bio-based and/or biodegradable materials with tailored properties. Similarly to starch, the improvement of the impact resistance of poly(lactic acid) has been one of the main objectives of its modification by using several types of biopolymers such as starch [14], polyurethane [56], natural rubber (NR) [57,58], tough polyhydroxyalkanoate copolymers [59–61] and polyesters including poly(butylene succinate) [62] and poly(ε-caprolactone) [63–67]. The brittleness of poly(3-hydroxybutyrate) is generally overcome by copolymerization with other hydroxyalkanoates of longer side-chains [16], thus blending is of secondary importance in this case. However, there are examples for the successful application of blending, which should not be ignored, since they can be advantageous both from the engineering and the economic point of view. We must emphasize that most of the blends mentioned above can be characterized with a low level of miscibility and interfacial interaction, resulting in inferior mechanical properties, thus they are seldom applied in practice without proper compatibilization.

We can conclude here that the large chemical variety of biopolymers open up unlimited possibilities for the modification of properties by blending. Interactions play a crucial role in the determination of the structure and properties of the blends. More thorough considerations and the study of miscibility–structure–property correlations are

needed to fully utilize the potentials of the approach. In spite of the polar character of biopolymers, often compatibilization is needed to achieve the properties required for a specific application.

5. Compatibilization

Compatibilizers generally exhibit interfacial activity in heterogeneous polymer blends [94], while the compatibilizing effect is usually attributed to an increase in interfacial adhesion and to smaller dispersed particles leading to improved mechanical properties. Different strategies of compatibilization can be distinguished. In the case of non-reactive methods premade amphiphilic compounds, like block-copolymers are added to the blend, one constitutive end or block being miscible with one blend component, while the other with the second component. The most significant representative of non-reactive compatibilization of biopolymer blends is the addition of block-copolymers [65–67,126–135]. The development of other methods like the incorporation of amphiphilic low molecular weight compounds [52], ionomers [50,136] or a third polymer at least partially miscible with both blend components [45] is in an initial phase and, in our opinion, of secondary importance. One of the main reasons for the lack of success of non-reactive compatibilization is that reactive methods are more efficient [94]. In this case, the blocky structures acting as compatibilizers form in situ during blending. This might involve the addition of polymers with reactive groups [34,37,53,58,137,138], or small molecular weight chemicals [37,40,139–142] to form the compatibilizer. Another possibility is the chemical modification of one of the components to create reactive groups on them [47,57,114,115,133]. The fact that biopolymers often contain various reactive groups makes the application of these methods plausible and convenient. In the following sections, we present a comparative summary of the compatiblilization techniques used for biopolymer blends.

5.1. Non-reactive compatibilization

The toughening of biopolymers by blending with elastomers, like PCL, has been extensively investigated. PCL is a biodegradable polymer with excellent deformability and impact properties, thus it is very much appropriate for the modification of brittle PLA. Unfortunately, the melt blending of these polymers results in marginal improvement of toughness at the price of a considerable decrease in stiffness and strength as a result of complete immiscibility and weak interfacial adhesion [64,66]. In order to improve compatibility and achieve a more advantageous combination of properties, several methods have been applied, e.g. the addition of block copolymers such as PCL–PLA diblock [128–130], triblock [128,131,132] and random copolymers, a PCL–PEG copolymer [65] and a PEO–PPO–PEO triblock copolymer [67] with various success.

A similar approach is applied for the non-reactive compatibilization of other biopolymer blends. Dextran-grafted polymers offer the possibility to modify interfacial adhesion and properties of polysaccharide-based materials like in TPS/PCL [133] and PLA/dextran blends [134]. Attempts

were also made to compatibilize the blends of biopolymers with commodity plastics using block-copolymers. The group of Hillmyer [126,127] used low density polyethylene (LDPE) for the modification of PLA in order to decrease material cost and to improve toughness. The addition of LDPE–PLA block-copolymers resulted in considerably increased deformability compared to the uncompatibilized blend, although the tensile strength of the blend was smaller than that of the neat PLA. Unlike PLA and LDPE, poly(3-hydroxybutyrate) and poly(methyl methacrylate) (PMMA) are miscible in a certain composition range. The use of a PHB-g-PMMA block copolymer as compatibilizer proved to be advantageous outside this range, the disappearance of a rapidly crystallizing PHB phase led to improved ductility in these blends [135].

Although compatibilization is a practical approach aiming the improvement of performance, the effect of modification on the mechanical characteristics of the blend is often neglected. Many authors draw conclusions about the efficiency of compatibilization from changes in thermal properties or morphology [131,132]. These are important parameters offering information about miscibility indeed, but successful compatibilization is related to changes in properties being advantageous for a certain range of applications. Unfortunately, physical compatibilization has its limitations, as Figs. 7 and 8 present graphically. Relative strength is plotted against the amount of compatibilizer for the same blend with and without compatibilization in Fig. 7, while relative elongation-at-break in Fig. 8. We may conclude from the figures that considerable and simultaneous improvement of deformability and strength is seldom achieved by physical compatibilization ($\square, \diamond, \bigcirc$),
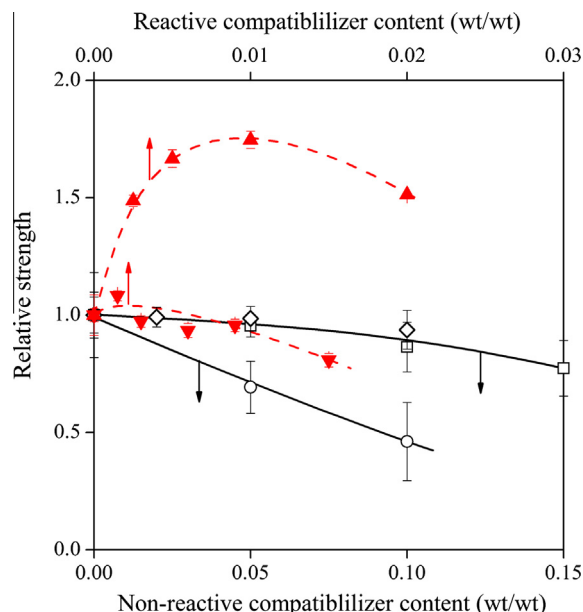

Fig. 7. Comparison of reactive and non-reactive compatibilization effect of additive content on the relative strength of PLA based blends; reactive compatibilization: PLA/starch 55/45 (▼) [40], PLA/poly(propylene carbonate 70/30 (▲) [141], non-reactive compatibilization: PLA/LDPE 80/20 ($\diamond$) [126], PLA/PCL 80/20 ($\square$) [65], PLA/PCL 50/50 ($\bigcirc$) [65].
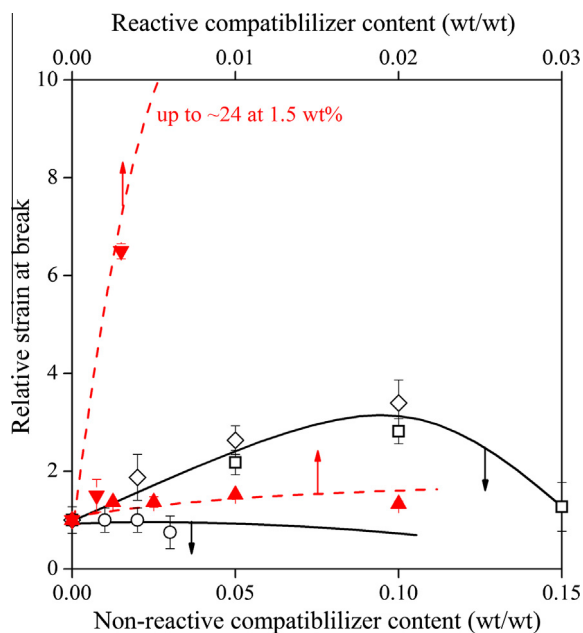
Fig. 8. Comparison of reactive and non-reactive compatibilization effect of additive content on the relative strain at break of PLA based blends; reactive compatibilization: PLA/starch 55/45 (▼) [40], PLA/poly(propylene carbonate 70/30 (▲) [141], non-reactive compatibilization: PLA/LDPE 80/20 (◇) [126], PLA/PCL 80/20 (□) [65], PLA/PCL 50/50 (○) [65].

while much larger effects are observed when reactive techniques are used (▲,▼). Although compatibilizer contents are difficult to compare in these two approaches, we must note that properties can be adjusted in a much wider range with reactive compatibilization, thus improving the application possibilities of biopolymer blends.

5.2. Reactive compatibilization

As mentioned above, biopolymers often contain a number of reactive groups offering excellent possibility for the reactive compatibilization of their blends. The addition of a compound miscible with one blend component and reactive towards the functional groups of the other results in the in situ formation of grafted or block-copolymers acting as compatibilizers. The method possesses considerable potentials, since structure and properties can be controlled relatively easily by the proper selection of agents, blend composition and processing conditions.

Compatibilization techniques consisting of multiple steps are described in a series of studies. This can be the chemical modification of one blend component in the first processing step followed by blending, during which no chemical reactions take place [47,57,114,115]. In this case, interactions in the blend, thus compatibility, might improve as a result of changes in the characteristics of the interface. This approach is very similar to the non-reactive methods, with the same limitations. However, if modification involves the formation of groups on one component which are able to react with the second component during blending, the phases can be coupled chemically. The grafting of polymers with anhydrides resulting in the formation of free acid groups is a typical example. The reactive polymers obtained are frequently used for the compatibilization of starch based blends containing a large number of hydroxyl groups. Among others, blends containing anhydride-grafted PCL [137,138], PLA [34,37] and PHB [143] have been prepared this way. In an interesting study, Hassouna et al. [29] synthesized block-copolymers in situ using maleic anhydride (MA) grafted PLA and hydroxyl terminated poly(ethylene glycol) in order to improve compatibility of PEG/PLA blends. Other functionalities like epoxy [58] or isocyanate groups [53] might also be used in various biopolymer based systems. Fig. 9 presents the effect of a reactive polymer, MA grafted polypropylene (MAPP), on the morphology of polypropylene (PP)/TPS blends. Addition of the coupling agent results in a significant decrease in the size of the dispersed particles (Fig. 9a) compared to the blend without compatibilization (Fig. 9b). Interactions and structure affect also the mechanical properties of the blends considerably. In uncompatibilized PP/TPS blends (□) the composition dependence of relative
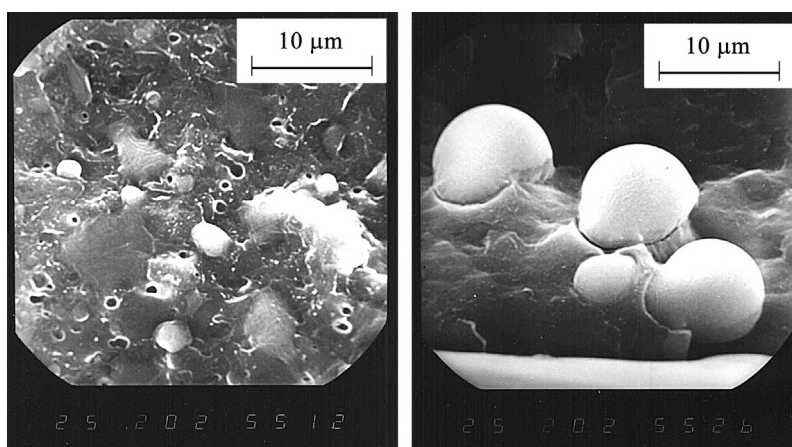

Fig. 9. Morphology of PP/TPS blends (a) with and (b) without the addition of a reactive polymer (MAPP) as compatibilizer.

tensile strength is far below additivity, close to the theoretical minimum (Fig. 10). Compatibilization (■) significantly improves strength as a result of stronger adhesion and smaller size of dispersed particles.

Unsaturated anhydrides, and maleic anhydride in particular, are often attached to biopolymers via radical reaction routes using different peroxide initiators. The technique was reported to be appropriate for the modification of various polyesters, either in solution, suspension, solid or melt state. Successful grafting and the structure of the reactive polymers were confirmed by FTIR and NMR spectroscopy [144]. In their study, Zhang and Sun [40] apply the technique described earlier by Carlson et al. [145] to graft PLA with maleic anhydride. The MA-grafted poly(lactic acid) is claimed to react with the hydroxyl groups of starch during blending resulting in the coupling of the phases according to the scheme shown in Fig. 11. Although properties were still inferior to that of neat PLA, cross-linking resulted in the considerable increase of strength in blends with the same composition (45 wt.% starch, see Figs. 7 and 8) thus in acceptable mechanical characteristics and significant cost-reduction. In the same study [40], two-step reactive compatibilization, i.e. modification of PLA followed by blending, had been compared to one-step reactive processing. Compatibilization effect was confirmed in this case as well.

Most authors using a similar approach agree that maleic anhydride is an effective compatibilizer in biopolymer blends. The underlying chemical processes, on the other hand, are extremely ambiguous. Several authors reported that MA reacts with both blend components forming block-copolymers, while others state that only the reaction with one component, i.e. the formation of maleated starch [140], can be confirmed and presumably secondary, physico-chemical interactions result in better compatibility in these systems.
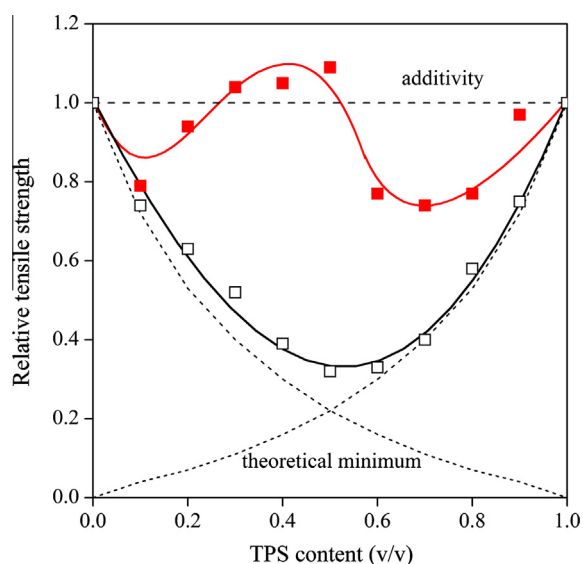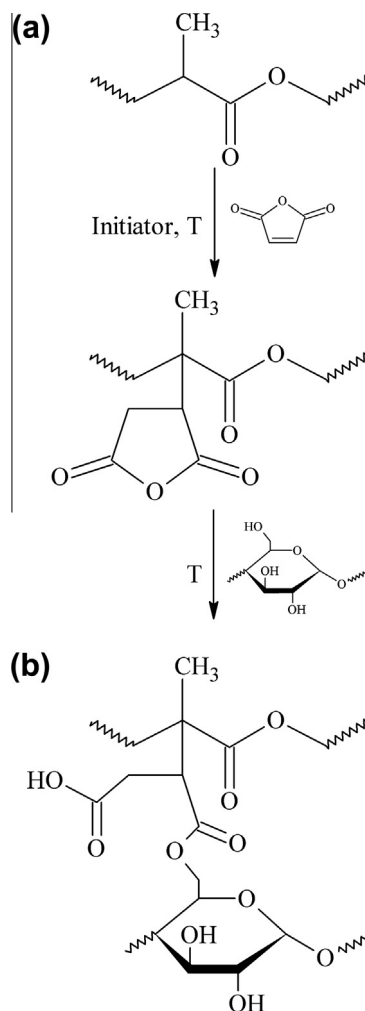
Fig. 11. Reactive compatibilization of PLA/starch blends: (a) free-radical grafting of PLA with maleic anhydride and (b) reaction with the hydroxyl groups of starch [40].

Nevertheless, one-step blending and compatibilization possesses several advantages, both from an economical and environmental point of view, since it enables the elimination of several processing steps. Considering the short processing times used, compatibilizers must be distributed at a high rate in the polymer melt during blending, thus usually small molecules [37,40,139–142] or lower molecular weight polymers [34,53,137,146] are applied. These should be able to react with both components to couple the phases. The appropriate reactivity of the components is also very important for the success of this approach [94]. Anhydrides are frequently used for this purpose as well [37,40,139,140,146], but the application of other compounds like diisocyanates [142] and epoxides [146] have also been reported.

Reactor blends represent a specific category among compatibilized biopolymer blends. These materials are produced by the synthesis of one polymer in the presence of another. Poly(acrylonitrile–butadiene–styrene) (ABS) is a well-known conventional example of this class of

Fig. 10. Composition dependence of relative tensile strength of PP/TPS (□) and compatibilized PP/TPS/MAPP (■) blends.

materials. The approach can also be applied to biopolymer blends. Such a process was reported by Dubois et al. [147,148] more than 10 years ago. The ring-opening polymerization (ROP) of cyclic esters initiated by the hydroxyl groups of biopolymers like starch [147], dextran [148] or partially substituted cellulose acetate (CA) [31–33] is a convenient method for the preparation of block copolymers via reactive processing, although various other combinations are also possible. Several groups have reported improved adhesion, morphology and mechanical properties in systems prepared by this approach. Fig. 12 presents the scheme for the grafting of partially substituted cellulose acetate with ε-caprolactone. The reaction is catalyzed by stannous octoate (Sn(Oct)$_2$). In the reported study ε-caprolactone (CL) was added in high excess during reactive processing, thus both grafted cellulose acetate and CL homopolymers formed in the reaction [31,32]. Although structure and interactions are difficult to characterize properly in these systems because of the competitive reactions during blending and because of the continuous migration of PCL fractions with small and medium molecular weights afterwards, unambiguous correlation can be observed between the length of CL side chains grafted onto CA (○) and the deformability (●) of the blends (Fig. 13).

In another work, the synthesis of a segmented polyurethane elastomer (PU) in PLA melt has been carried out in order to improve the impact resistance of this latter polymer. The basic idea was the coupling of the components through the isocyanate group reacting with the hydroxyl and carboxyl end-groups of poly(lactic acid), which results in the formation of grafted PLA-g-PU copolymers acting as compatibilizer (Fig. 14). The properties of the reactor blend were compared to those of samples with the same composition but prepared by physical blending (PLA/PU). Although the research is still in its initial phase, preliminary results are promising. The dispersion of PU in blends

containing PLA-g-PU is better; the average diameter of particles is considerably smaller in them (●) than in physical blends (○) (Fig. 15). Mechanical characteristics (Fig 16) also show the benefits of reactive processing. A parameter (C) related to the stress transfer between the phases can be calculated from the composition dependence of tensile strength using the approach described in Section 4.4. As Table 2 shows, interactions are stronger in PLA-g-PU blends indicating the successful reactive compatibilization of PLA and the polyurethane elastomer.

Reactive techniques are versatile and offer very effective ways to compatibilize biopolymer blends. The chemical structure of these materials also supports the application of this approach. Several questions regarding the underlying molecular processes and reaction mechanisms as well as their effect on macroscopic properties are to be answered yet, thus further development can be expected in this field.

6. Application

The application of biodegradable polymers is possible and advantageous only in a few areas, mainly in packaging and agriculture, although medical applications of certain types can be also important as described later in this section. The interest in this latter area is large and further increase is expected. As Table 3 indicates, commercial grades of fully biopolymer blends have found already application in the former two areas. In short service life applications, the environmental advantage, i.e. the compostability of the products is the most important requirement fulfilled by all of these grades. They are mainly starch or PLA based materials modified by blending with different types of polyesters, e.g. aliphatic–aromatic copolyesters (AACs). For long-term applications, however, degradability is either of secondary importance or even disadvantageous, thus several hybrid blends based on starch and poly(lactic
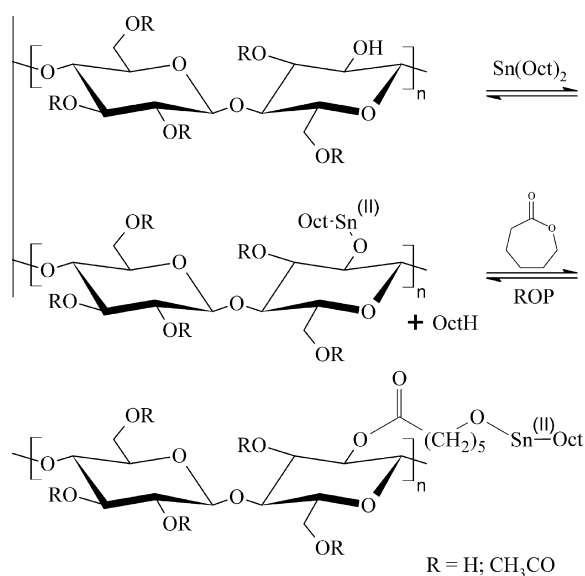

Fig. 12. Ring opening polymerization of ε-caprolactone initiated by the hydroxyl groups of partially substituted cellulose acetate [31,32].
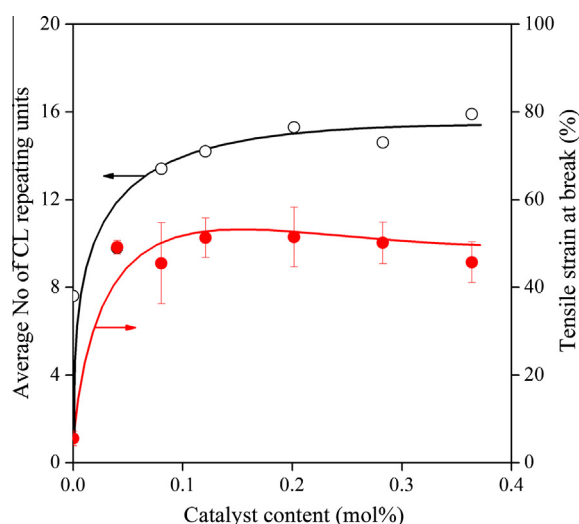

Fig. 13. Grafting of cellulose acetate with ε-caprolactone. The effect of catalyst content on the length of CL side-chains and the deformability of the blends.
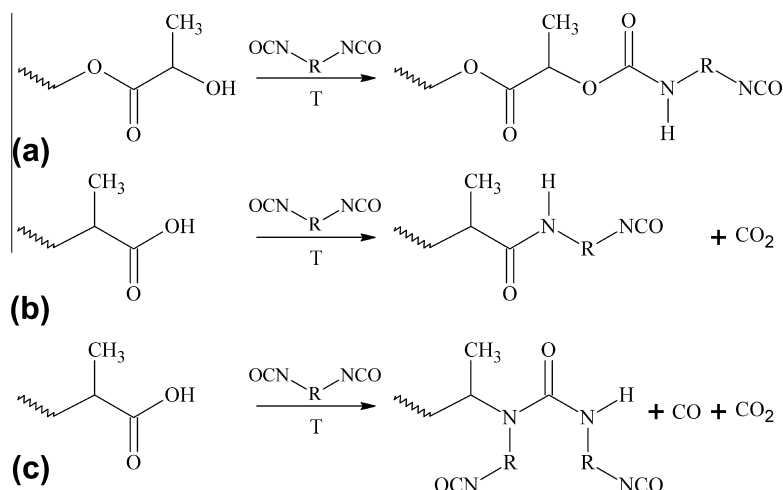
Fig. 14. Reaction of a diisocyanate with PLA end-groups: (a) formation of polyurethane on the hydroxyl end-group; (b) formation of amide on the carboxyl end-group; and (c) formation of acylurea on the carboxyl end-group.
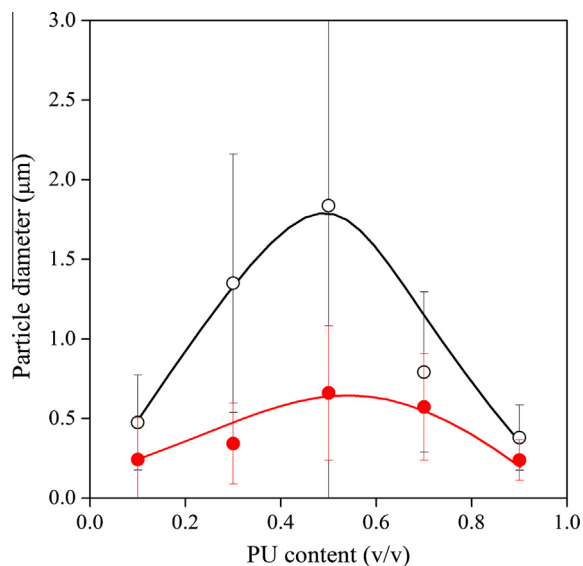

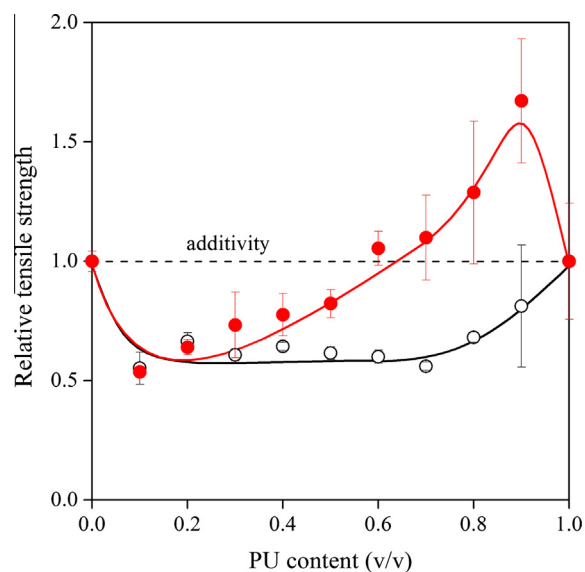**Fig. 15.** Composition-dependence of particle size in physical (PLA/PU, ○) and reactor blends (PLA-g-PU, ●).

Fig. 16. Effect of the addition of a polyurethane elastomer on the mechanical characteristics of PLA. Comparison of physical (PLA/PU, ○) and reactor blends (PLA-g-PU, ●).

acid), which contain conventional and biopolymers are present on the market. In the case of such blends, the renewable content of the raw materials is emphasized. The progress towards the utilization of renewable feedstock for the production of polymeric materials is a favorable trend irrespectively of the intended application, since the synthesis of several conventional as well as most biodegradable polymers is possible on the basis of feedstock derived from natural resources. Starch is often modified with commodity polymers and polyolefins in particular. As these materials are not compostable, the real advantage of using such grades is ambiguous. PLA based hybrid systems, on the other hand, are usually developed for applications demanding better performance, thus they are

Table 2
Comparison of PLA–PU physical and reactor blends.

Material	Relative load bearing capacity (B)	Stress transfer (C)
PLA/PU	2.31	17.0
PLA-g-PU	3.43	52.3

generally produced from engineering polymers. The advantage of such materials might be the increased renewable content and even the relative high price of PLA can be better tolerated in these application areas. However, the attention must be called here to the fact that most biopolymer based blends available on the market are

Table 3
Representative commercial grades and application areas of biopolymer blends.

Components		Targeted application area	Brand name	Supplier
Biopolymer blends				
Starch	Aliphatic polyesters	Packaging, agriculture	Bionolle Starcla	Showa Denko
Starch	Aliphatic polyesters	Packaging	Biograde	Biograde
Starch	Co-polyester	Consumer goods, packaging, agriculture	Terraloy	Teknor Apex
Starch	AAC	Packaging, agriculture	Biolice	Limagrain
Starch	AAC	Packaging	Compostables	Cereplast
Starch	AAC, PCL	Consumer goods, packaging, agriculture	Mater-Bi	Novamont
PLA	Co-polyester	Consumer goods, packaging, agriculture	Bio-Flex	FKuR
PLA	AAC	Packaging	Compostables	Cereplast
PLA	AAC	Packaging	Ecovio	BASF
Hybrid blends				
Starch	PP	Consumer goods, packaging, automotive	Biopropylene	Cereplast
Starch	PE, PP	Packaging	Cereloy Eco	Cerestech
Starch	PE, PP	Consumer goods, packaging, coatings	Cardia Biohybrid	Cardia Bioplastics
Starch	PE, PP	Packaging	Biograde	Biograde
Starch	PE, PP, HIPS	Consumer goods, packaging, agriculture	Terraloy	Teknor Apex
PLA	ABS	Consumer goods, packaging, electronics	Biolloy	Techno Polymer
PLA	PE, PC, PMMA, ABS	Consumer goods, automotive, electronics	RTP 2099 X	RTP
PLA	Engineering thermoplastics	Consumer goods, automotive, electronics	reSound	PolyOne

compatibilized. The use of blends containing immiscible and incompatible polymers is impossible otherwise, which again indicates the importance of these techniques.

Advanced biomaterials, and biopolymer blends in particular, are being used in increasing quantities in biomedical applications in various forms replacing traditional engineering materials, the characteristics of which generally fail to meet the high standards of modern human healthcare. One critical function of biomaterials is biocompatibility, i.e. to bridge the interface between artificial and biological systems thus promoting favorable cellular interactions and tissue development. Ideal biomaterials should also be biodegradable and bioresorbable, easy to be sterilized and non-toxic, which applies to their degradation products as well, while maintaining adequate mechanical and physical properties during their degradation to support the reconstruction of a new tissue without inflammation [149]. Consequently, degradation rate and mechanism should be adjusted exactly to the desired application.

Significant areas where advanced biomaterials are applied involve the production of nano- and micro-particles for drug delivery and controlled release applications [150], two-dimensional structures, e.g. membranes for wound dressing [151], porous matrices (scaffolds) for tissue engineering purposes, to support cells and promote their proliferation [152]. Such structures generally consist of a responsive layer immobilized on a polymer substrate, the former ensuring adequate biocompatibility and convenient removal of the cells. Although there are innumerous studies related to responsive polymeric materials, the development and investigation of the substrates are much more neglected areas. These materials have to meet extremely challenging requirements: biocompatibility, tailored mechanical properties, easy sterilization, controllable and interconnected porosity, near-net-shape fabrication and scalability for cost-effective industrial production [153]. Multi-component, heterogeneous polymeric systems, blends [154–156], micro- [153] and nano-composites [157] play an important role in answering such complex

expectations, as the properties of these can be conveniently adjusted with the proper selection of the components and their concentration, processing techniques, etc.

Natural-based polymers and their blends are frequently studied and applied in the biomedical area [152,155,156, 158–160], for these offer the advantage of being similar to biological macromolecules, while their properties are generally comparable with those of the extracellular matrix leading to less inflammation, immunological reactions and toxicity [152]. Many studies aim to combine the biological properties of natural polymers with the favorable thermal and mechanical characteristics of synthetic ones [158–160]. Recent studies include various biomaterials like poly(lactic(acid)/calcium-alginate [155], poly(vinyl alcohol)/gelatin [159], polyurethane/chitin [160] blends.

During the discussion of the biomedical application of polymers, hydrogels must also be mentioned. These are insoluble, highly swellable hydrophilic polymeric systems used as selective membranes [161], scaffolds [162] and drug-delivery systems [163]. Due to their high water content, they are very soft materials with viscoelastic properties similar to that of the living tissue [164] and they can be fabricated to be flexible, durable, and permeable to metabolites. The characteristics of hydrogels are determined by the type of the polymer, crosslink density, chain length and the degree of swelling [162]. Although various combinations of different, natural and synthetic, biopolymers are applied to form hydrogels, they are mostly copolymers [162], as the biopolymer blocks are covalently bonded, thus these materials are outside the scope of our present article.

7. Conclusions

Biopolymers are in the center of attention, their production and use increases continuously at a very high rate. However, they are surrounded with much controversy and even terms used in the area need further clarification.

Biopolymers themselves, both natural polymers and plastics produced from natural feedstock by synthetic routes, often have inferior properties compared to commodity polymers. Modification is a way to improve properties and achieve property combinations required for specific applications. Blending is one of the approaches to modify the properties of biopolymers; the impact strength of inherently brittle polymers, mainly aliphatic polyesters, can be improved considerably by the approach. Further study is needed on the miscibility–structure–property relationships of these materials to utilize all potentials of blending. Their chemical structure opens up possibilities to the reactive modification of these polymers. Copolymerization, grafting, trans-esterification, the use of reactive coupling agents have all been utilized with success to achieve polymers and blends with advantageous properties. The possibilities are unlimited and further progress is expected in the field. Biopolymers and their blends are applied successfully in several areas already.

Acknowledgements

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